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Phosphorus recovery from the biomass ash: A review

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A R T I C L E   I N F O

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A B S T R A C T

Biomass ash, generated during the thermal chemical conversion of biomass for energy production, is an industrial by-product which is often recognized as a solid waste, but there are some useful elements in the biomass ash such as phosphorus, etc. So through some technology and methods, the biomass ash can be transferred into a useful resource. The paper mainly includes the following aspects: biomass ash composition characteristics, biomass thermal chemical conversion for phosphorus and phosphorus recovery technology from biomass ash. Through these aspects literature review, not only the whole biomass ash characteristics was made clear, but also we think that the idea of phosphorus from biomass ash is feasible, especially for some high phosphorus ash such as sludge ash, meat and bone meal (MBM) ash, etc. So the review about phosphorus from the biomass ash is very important practical significance for biomass energy, biomass ash disposal and phosphorus resource.

Contents

1. Introduction

During the last years, an increasing interest for sustainable energy production has been seen globally. This development is mainly caused by the international concern regarding CO_2 emissions. Biomass fuels are CO_2-neutral and their use for energy production could substantially decrease the greenhouse effect at a global level [1,2]. Thermo-chemical technologies, especially in the form of combustion are thought to be promising solutions for energy production from biomass. Its most advanced form is considered to be fluidized bed combustion [3–5]. Biomass fuels usually have a high content of alkali metals, which, together

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with other mineral components of the ash, give rise to severe ash deposition. Ash deposition can reduce the heat transfer and increase the boiler tube corrosion [6–8]. Although biomass ash can produce some disadvantages, due to some biomass ash such as olive ash, sludge ash, meat and bone meal (MBM) ash, etc. containing a large of valuable nutrient element such as phosphorus and potassium, people can reuse biomass ash for recovery nutrients. Especial for P, the merging of food and fuel economies has increased the demand of mineral P fertilizer, and its price increased over 200% in 2007 [9,10]. So about P recovery from biomass ash is also very important for biomass energy utilization.

Apatite minerals are the main raw materials used in the manufacturing of fertilizers. However, the resources of apatite in the world are estimated to last only for about 200 years. Therefore, sustainable methods to recycle the phosphorus used in the society are needed [128]. Phosphorus is a limited non-renewable resource, which is indispensable as an essential nutrient for the growth of organisms in most ecosystems, and cannot be replaced by other elements. It is a very important element for many industries as well. The demand for phosphorus fertilizer alone increased with the increase in the world's population from 9×10^6 to 40×10^6 metric tons between 1960 and 2000 and was expected to increase further to 20×10^6 metric tons by 2030 [123]. Phosphorus, being a limited natural resource, is used in the industry in many different applications. As primary phosphorus compounds in sewage sludge constituents of organic origin were identified. The wastewater de-phosphorization by the biological cleaning stages enriches the phosphorus concentration in the organic residues, mostly as adenosintriphosphate (ATP). A share of approximately 10% is bound in stable iron or alumina phosphates during the chemical precipitation step [130]. Generally, the phosphorus is enriched in the fly ash together with the trace elements. An important issue in the development of sludge ash utilization strategies is whether the concentration of trace elements is low enough to allow the use of sludge ashes or products thereof as fertilizers [126]. The ash has a relatively high P content (approximately 5.4% by weight) and could therefore, with advantage be recycled as a P fertilizer on agricultural land. Recycling of P is especially important seen in the light of the shrinking global phosphate rock reserves and increases in demand for P fertilizer in agriculture [124,125]. In MBM, a significant share of the phosphates is hydroxyapatite, the major constituent of bones. A percentage of approximately 10% is also organically bound phosphates similar to sewage sludge. Due to the low boiling points of organic phosphorus compounds, it is assumed that these are released as gaseous phosphorus oxides in the boiler. The phosphorus oxides condense in the temperature range of 400–600 °C, forming primarily phosphorus-oxide, P_4O_{10}, and, in the likely presence of water, orthophosphoric acid, H_3PO_4 [131]. As an alternative to phosphorus rock, phosphorus can be recycled from phosphorus-rich residues, such as meat and bone meal (MBM), municipal sewage sludge, phosphorus-rich ashes, agricultural residues, etc.[128]. The plant nutrients such as phosphorus, potassium, magnesium, and sodium, are nearly completely recovered in the agriculturally usable ash-mixture of bottom ash and cyclone fly ash. Thus, returning the ash to the grassland could close the cycles of these nutrients [127].

The objectives of this paper were to: (1) research a variety of bio-fuels and its ash composition characteristics, so that we have a general understanding of the composition of bio-fuel and its ash as the base of ash research; (2) systematically summarize and analysis phosphorus characteristics in bio-fuel ash from the biomass thermal conversion technology; (3) examine these potential technologies for P recovery from the biomass ash.

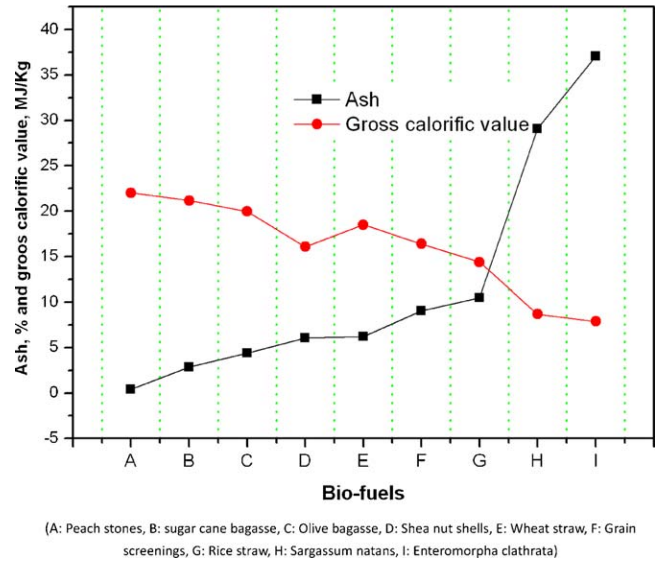


Fig. 1. Gross calorific value trend following the ash content adding in the different fuels.

2. Bio-fuel composition analysis

Several typical bio-fuels are investigated about their composition. The ultimate analysis of different fuels is shown in Table 1. From Table 1, we can know some characteristics about the bio-fuels composition. The first, comparing to the coal, carbon content of biomass fuels is less. The highest carbon content of biomass fuels is about 53%, equivalent to the carbon content of lignite which was generated from the less age. The fixed carbon content of biomass fuels is also significantly less than the coal. Therefore, they are no resistances to burn, the lower heating value than the coal. The second, biomass fuels are hydrogen content higher, obviously more volatile. Carbon and hydrogen together form the majority of low-molecular weight hydrocarbons in the biomass fuels, which are decomposed into volatile compounds out of the fold when they meet a certain temperature. Therefore, biomass fuels are easily ignited, burning, and the black side flame is easy to produce. The third, biomass fuels are more oxygen. Obviously the oxygen content of biomass fuels than coal, which makes the low heat value of biomass fuels, but the easy ignition. When burned, they can be a relative less in the supply air volume. The fourth, biomass fuels are low sulfur content. Most biomass fuels with sulfur content are less than 0.30% except manure, which are beneficial to environmental protection. The last, seen from Table 2 and Fig. 1, biomass ash content is close related with the gross caloric value. Under normal conditions, with the ash content increased, the gross calorific value of biomass fuels is to reduce, but not a direct proportion relationship.

3. Bio-fuel ash composition characteristics

3.1. Ash composition properties from bio-fuel combustion

The biomass fuel ash composition influences boiler ash deposit formation and agglomeration, boiler tube corrosion, and ash use. Table 3 shows the chemical composition of some typical biomass ashes which data are from the literature. From Table 3, we can know that the ash mainly include K, Na, Ca, Mg, Si, P, Al, Fe, S and so on elements, especially for alkali metal and alkali earth metal content prominent. To make a better comparison of the different fuel ashes possible, we have used a classification system which is based on the

Table 1
Ultimate element analysis of the different bio-fuels.

Element	C	H	N	S	O
Wheat straw 1 [11]	43.2	5.6	1.0	0.18	50.02
Wheat straw 2 [12]	40.78	5.84	0.178	0.283	52.919
Wheat straw 3 [13]	44.8	7.01	0.56	0.17	47.46
Wheat straw 4 [21]	46.95	5.355	0.506	0.222	39.7
Wheat straw (average)	43.9325	5.95125	0.561	0.21375	47.52475
Rice straw 1 [14]	39.64	4.64	0.72	0.11	36.36
Rice straw 2 [15]	39.20	4.84	1.6	0.67	53.69
Rice straw 3 [16]	39.6	5.8	0.7	0.2	53.7
Rice straw 4 [17]	35.37	4.82	0.96	0.14	39.15
Rice straw (average)	38.4525	5.025	0.995	0.28	45.725
Sugar cane bagasse 1 [18]	42.64	6.62	0.19	0.07	50.48
Sugar cane bagasse 2 [20]	42	6.58	0.26	0.16	51
Sugar cane bagasse 3 [22]	46.9	5.5	0.2	ND	47.4
Sugar cane bagasse 4 [23]	45.45	5.26	0.23	0.05	36.65
Sugar cane bagasse (average)	44.2475	5.99	0.22	0.07	46.3825
Olive bagasse 1 [19]	51.6	8.5	1.1	ND	35.7
Olive bagasse 2 [21]	53.4	7.5	1.7	ND	37.4
Olive bagasse 3 [24]	53.4	7.46	1.7	ND	37.44
Olive bagasse (average)	52.8	7.82	1.5	ND	36.84667
Manure 1 [25]	51.7	5.8	5.9	0.8	35.9
Manure 2 [26]	49.66	6.64	4.71	0.66	38.33
Manure (average)	50.68	6.22	5.305	0.73	37.115
Sewage sludge [141]	42.0	6.0	6.0	0.9	43.2
Sewage sludge [142]	38.2	4.3	4.5	0.9	20.9
Sewage sludge [142]	22.7	3.3	3.1	1.6	15.5
Sewage sludge (average)	34.3	4.53	4.53	1.13	26.53
Paper mill sludge [138]	37.84	4.87	0.35	0.10	28.01
Paper mill sludge [139]	18.45	2.10	0.82	0.16	13.27
Paper mill sludge [140]	23.0	2.8	1.7	0.1	21.3
Paper mill sludge (average)	26.43	3.25	0.95	0.12	20.86
Coal 1 [27]	72.1	3.60	1.36	0.35	8.01
Coal 2 [28]	69.9	5.5	0.94	0.31	23.35
Coal 3 [29]	79.1	4.6	0.9	1.3	14.1
Coal 4 [30]	68.42	3.91	1.32	0.7	12.69
Coal (average)	72.38	4.4025	1.13	0.665	14.5375

content of alkali metal and alkali earth oxides, silicon oxide, and phosphorus oxide according to ash composition characteristics in Table 3. Different fuel ash are placed in the triangular diagram by assuming the ashes are composed solely of K_2O, Na_2O, MgO, CaO, SiO_2 and P_2O_5. By placing the typical bio-fuel ash in the triangular diagram, as shown in Fig. 2, it is possible to make clear the ash element distribution. From Fig. 2, we will divide the triangular diagram into A, B, C and D, four groups. Group A includes most fuels which are explained that the content of alkali and alkali earth metal oxides is more than 50%, so most bio-fuel ash has a lot of alkali and alkali earth metal which can produce the ash deposit problem. From Fig. 2, we can know that the Si is also main element in the bio-fuel ash. Like 1, 2, 3, 4 and 12 in the group B, the Si content is more than 50%, so the Si is also rather important element in the biomass fuel ash. In particularly, the reacting relationship of Si and alkali metal will directly influence the bio-fuel ash deposit and agglomeration problem. In the group C, the P content is prominent about 50% like 10. P is an important nutrient element and P resource in the world is more and shorter, so I think that, like these rich P ash, we should consider how to recover P from them. The last group D, Si, P and alkali metals are more average about 30%. Like this, there is almost no in the bio-fuels.

Table 2
Ash and gross calorific value of the different bio-fuels.

		Ash, %	GCV, MJ/kg
A	Peach stones [31]	0.38	22.02
B	Sugar cane bagasse [19]	2.84	21.162
C	Olive bagasse [24]	4.42	19.97
D	Shea nut shells [32]	6.06	16.059
E	Wheat straw [32]	6.22	18.5
F	Grain screenings [33]	9.02	16.397
G	Rice straw [17]	10.46	14.4
H	Sargassum natans [34]	29.09	8.68
I	Enteromorpha clathrata [35]	37.09	7.89

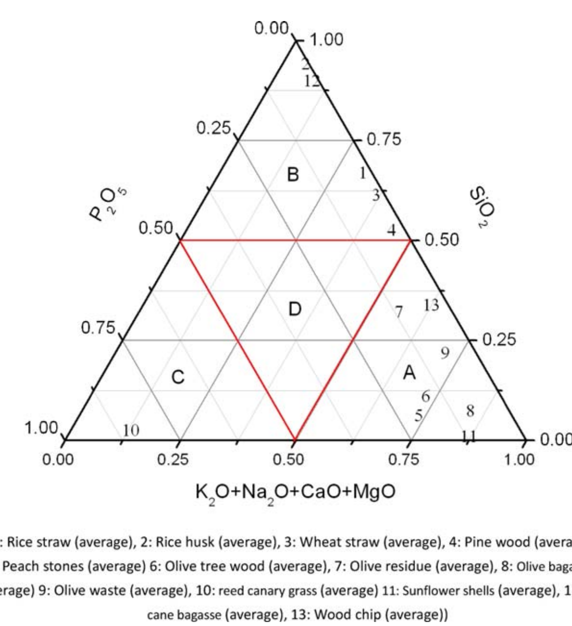


Fig. 2. Triangular diagram representing the chemical composition of biomass fuel ashes.

Table 3
Ash elemental analyses of different fuels.

Sample	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	P2O5	SO_3
Rice straw A [33]	15.3	0.4	3.5	1.6	69.9	0.3	0.2	1.5	No
Rice straw B [39]	19.4	1.98	10.12	2.47	56.23	1.94	0.98	1.93	4.95
Rice straw C [14]	13.56	0.42	1.65	1.49	72.23	0.07	0.22	1.86	0.86
Rice straw D [40]	38.92	2.16	9.23	1.96	44.72	1.13	0.14	1.63	No
Rice straw E [49]	11.95	0.14	1.6	1.64	75.38	0.09	0.10	0.61	No
Rice straw F [50]	16	2.8	8.9	3.5	51	No	No	No	No
Rice straw (average)	19.18	1.31	5.83	2.11	61.57	0.70	0.32	1.50	2.90
Rice husk A [55]	6.2	No	1.92	No	66.3	0.064	0.78	0.07	No
Rice husk B [56]	1.9	0.01	0.6	0.3	95.9	0.1	0.1	0.6	No
Rice husk C [56]	1.8	0.01	0.4	0.3	95.4	0.1	0.05	No	No
Rice husk (average)	3.3	0.01	0.97	0.3	85.86	0.08	0.31	0.33	No
Wheat straw A [41]	21.04	1.65	3.32	2.33	60	1.73	0.89	1.24	3.8
Wheat straw B [34]	23.99	5.22	2.7	1.73	27.96	3.43	0.59	No	3.83
Wheat straw C [49]	16.55	0.8	2.8	1.82	57.47	0.77	0.39	1.05	No
Wheat straw D [50]	18	0.22	8.1	2.4	44	No	No	No	No
Wheat straw (average)	19.89	1.97	4.23	2.07	47.35	1.97	0.62	1.14	3.81
Pine wood A [51]	10.04	0.17	51.3	8.00	14.45	2.71	1.61	2.82	No
Pine wood B [50]	7.9	1.9	13	4.5	52	No	No	No	No
Pine Wood C [36]	4.49	1.19	7.85	2.42	67.84	7	5.42	1.55	No
Pine wood (average)	7.47	1.08	24.05	4.973	44.76	4.85	3.51	2.18	No
Peach stones A [44]	45.78	0.07	6.13	1.4	5.03	0.47	0.63	No	5.09
Peach stones B [46]	43.6	0	16.16	0.3	5.16	7	5.42	15.39	5.04
Peach stones (average)	44.69	0.035	11.145	0.85	5.095	3.735	3.025	15.39	5.06
Olive tree wood A [52]	19.9	2.9	32.8	2.4	8.1	1.6	0.7	8.5	2.1
Olive tree wood B [53]	7.2	2.6	44.2	3.5	10	1.2	1.0	17.0	6.8
Olive tree wood (average)	13.55	2.75	38.5	2.95	9.05	1.4	0.85	12.75	4.45
Olive residue A [45]	27.23	4.18	10.21	3.79	32.6	2.95	1.9	No	4.97
Olive residue B [47]	21.67	3.23	12.8	5.71	31.41	3.94	2.6	No	3.1
Olive residue C [48]	12.94	7.24	22.77	6.73	23.54	2.33	5.43	No	2.85
Olive residue D [51]	9.18	0.93	22.9	3.77	45.05	6.98	6.24	2.36	1.57
Olive residue E [52]	24.7	3.4	22.0	3.0	10.7	2.7	1.7	14.7	3.5
Olive residue F [53]	12.7	4.3	32.9	4.8	20.4	4.4	2.6	11.1	4.8
Olive residue (average)	18.07	3.88	20.59	4.63	27.28	3.88	3.41	9.38	3.46
Olive bagasse [43]	51.6	No	23.3	2.3	7.1	1.9	No	7.5	2.5
Olive waste [38]	36.0	0.6	11.0	7.1	17.0	2.5	2.2	4.9	2.9
Reed canary grass [37]	3.4	0.9	5.6	1.2	2.5	1.3	0.7	72.5	No
Sunflower shells [31]	45.1	0.2	16	13.1	1.1	0.5	0.9	10.1	11.7
Sugar cane bagasse [42]	3.46	0.12	2.15	1.65	78.34	8.55	3.61	1.07	No
Wood chip A [35]	6.9	0.9	22.5	4.0	31.7	6.8	3.4	2.6	No
Wood chip B [49]	10.72	0.39	32.06	4.93	9.35	3.12	1.14	3.13	No
Wood chip C [17]	2.96	1.95	19.59	5.7	29.2	14.63	8.89	1.03	13.23
Wood chip D [54]	5.57	0.63	41.16	4.47	20.07	9.26	2.36	2.34	4.02
Wood chip (average)	6.53	0.96	28.82	4.77	22.58	8.45	3.94	2.27	8.62
Sewage sludge A [132]	2.34	0.82	5.61	1.4	43.6	16.6	10.4	12.1	0.24
Sewage sludge B [133]	1.7	1.0	20.6	1.9	34.2	12.6	4.7	14.8	2.8
Sewage sludge C [133]	2.52	0.79	1.93	1.45	64.95	15.21	6.95	1.51	–
Sewage sludge D [134]	1.93	0.67	1.05	0.13	43.2	13.2	12.6	17.4	1.99
Sewage sludge E [135]	1.70	0.32	1.93	1.48	50.6	12.8	7.21	1.67	2.38
Sewage sludge (average)	2.038	0.72	6.224	1.272	47.31	14.082	8.372	9.496	1.852
Paper sludge ash [136]	–	0.6	33.2	4.5	35.9	22.8	0.9	–	–
Paper sludge ash [137]	0.2	0.1	27.1	7.1	32.6	27.3	0.7	0.9	–
Paper sludge ash [138]	0.37	1.11	4.16	1.81	60.65	28.56	0.75	0.22	0.64
Paper sludge ash [139]	0.1	0	33.7	3.0	22.7	17.9	0.6	0.3	0.7
Paper sludge ash (average)	0.16	0.45	24.54	4.10	37.96	24.14	0.73	0.47	0.67

3.2. *Influence of combustion temperature on bio-fuel ash composition*

Knowledge of the retention or volatilization of alkali metal and other elements in ash during combustion of biomass fuels is important for efficient and economically viable large-scale biomass utilization because the major ash forming elements such as alkali metals (K, Na), alkaline earth metals (Ca, Mg), silicon, chlorine and sulfur can produce the bed agglomeration in CFB [57]. Among these ashes forming element in Table 4, potassium is the alkali metal present in significant concentration and its volatilization during firing is directly linked to formation of tenacious surface deposits. From Fig. 3, we can know that K concentration in ash increases at low temperature, and then reduces following the temperature increasing for the four biomasses. In Fig. 3, K content in ash starts to reduce from about 800 °C for the wood, rice straw and wheat straw except for the olive residue which starts to reduce from 600 °C. Due to K volatilization in ash at low temperature, K can react with SiO_2 in the bed particles in the CFB, and produce the potassium silicates which is the first melting point as low as some 750 °C so as to form a sticky layer in the surface of the bed particles, and then the bed agglomeration happens by the each bed particles. From these data analysis from the literatures, the result of agglomeration is the same as the mechanism of the “coating-induced” agglomeration.

Now let us look at Na element behavior, in Fig. 3, for the olive residue and wheat straw, following the temperature rising, the Na contents increase in the ash. So Na does not attend the reaction with the bed particles for the two biomasses. With regard to rice straw and wood, the Na contents in ash firstly increase, and then reduce at the beginning of about 1000 °C with the temperature rising. This change process is the similar to the K, but K contents reduce from the 800 °C which temperature is lower than the combustion

Table 4
Element compositions of different temperature in the common biomass ashes.

Sample	T	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	P_2O5
Wood [49]	1525	6.96	0.35	45.55	7.35	12.76	6.87	1.48	4.38
	1011	12.97	0.49	39.25	6.05	12.35	3.66	1.37	3.92
	816	13.34	0.49	39.03	6.03	11.72	3.71	1.32	3.85
	524	10.72	0.39	32.06	4.94	9.35	3.12	1.14	3.13
Wheat straw [49]	962	17.71	0.98	3.17	2.15	66.91	0.94	0.46	1.18
	816	18.85	0.92	3.12	2.10	65.45	0.91	0.44	1.17
	621	18.57	0.87	2.97	1.98	62.88	0.77	0.34	1.10
	524	16.55	0.80	2.80	1.82	57.47	0.77	0.39	1.05
Rice straw [49]	1325	10.06	0.16	2.34	2.01	83.12	0.13	0.09	0.49
	1011	11.35	0.21	2.21	1.93	79.90	0.12	0.12	0.67
	816	12.48	0.19	2.11	1.84	76.90	0.11	0.09	0.64
	524	11.33	0.16	2.00	1.74	72.55	0.11	0.08	0.60
Olive kernel [53]	900	12.7	4.3	32.9	4.8	20.4	4.4	2.6	11.1
	780	19.9	4.1	28.7	4.2	15.0	3.1	2.3	11.6
	600	24.7	3.4	22.0	3.0	10.7	2.7	1.7	14.7
Olive tree wood [53]	900	7.2	2.6	44.2	3.5	10	1.2	1.0	17
	780	12.7	2.7	43.4	2.8	9.2	1.5	1.9	12.7
	600	19.9	2.9	32.8	2.4	8.1	1.6	0.7	8.5

temperature of CFB. However the Na's releasing temperature is about 1000 °C which is more than the average combustion temperature. At the same time, we pay attention to Na content that is significantly lower than K content. So about the problem of bed agglomeration of biomass combustion, Na's contribution is small. To Ca, Mg, Si, Al and Fe element, their contents in the ash increased with temperature rising, so they have no contributions for ash agglomeration. In summary, about biomass ash agglomeration problem, K element is critical and other elements are secondary.

P element is the main nutrients for crop. However the P resource is increasing lack. In Fig. 3, P is enriched in the ash following the temperature rising except for the olive residue which P content decreases slightly. Therefore, to CFB combustion temperature is lower than 1000 °C, most of biomass combustion can make the P element to retain in the ash. This is good news for P recovery from the high P bio-fuels. To the slagging problem, what role does P play? Lindstrom et al. [58] think that high P bio-fuels can decrease the slagging trend because the ash is consisted of high-melting crystalline phases (calcium/magnesium potassium phosphates) during the combustion. So the P in the ash is help for avoiding the slagging problem.

3.3. Influence of leaching pre-treatment on bio-fuel ash composition

The major biomass combustion problem encountered in fluidized beds is bed agglomeration which is produced from the alkali metals. From Fig. 3, we know that the most important alkali metal is K element for the problem. Leaching technology is considered to be a low-cost pretreatment technique for the elimination of ash related problems in biomass combustion. From Fig. 4 and Table 5, we can know that through leaching, the K content in ash is obviously decreased for the four common biomasses. This can enhance the bio-fuel melting point and reduce the slagging trend in ash. For other elements' contents like Ca, Mg, Si, Al and Fe are either little change or a slight increase in the ash, but these elements for ash-related problem is secondary during the combustion process because they hardly volatilize in the high temperature in Fig. 3. Na element is also reduced like K, which is help for avoiding the ash slagging problem. By means of leaching, P content in the different kind biomass lowers which is not good for helping to solve the bed agglomeration because potassium phosphates can add the ash melting point and prevent the K volatilization to react the bed materials, but after the leaching ash the K content has already greatly reduced, so P contribution for agglomeration is not important during the combustion process. As P is a significant nutrient element for the crop, on the contrary, from another angle P can be recycled too well by the leaching technology. For the S and Cl, from Fig. 4, the two elements' content is also reduced, which is good news for the slagging because chloride and sulfate are easy to volatize. Therefore, leaching technology is a good means for avoiding the bed agglomeration during the bio-fuel combustion.

4. Bio-fuel ash deposit properties

4.1. Bio-fuel agglomeration temperature

Seen from Fig. 5 and Table 6, the initial agglomeration temperatures for most of bio-fuels were from 900 °C to 1000 °C. Among these bio-fuels, the highest initial agglomeration temperature is 1020 °C for baggasse sugar cane and rapeseed meal, and the lower initial agglomeration temperatures are respectively alfalfa, wheat straw and Lucerne. So seen from the whole initial agglomeration temperature situation, bio-fuels are easy to agglomerate because the normal operational temperatures in the interval of 800–900 °C and the burning particle excess temperatures of 20–200 °C that are considered as relevant for fluidized bed operation. Therefore, from biomass burning point of view, a single bio-fuel burning is not appropriate and easy to agglomerate, while the co-combustion would be beneficial. Through the mixing other fuels, it can improve the initial agglomeration temperature of bio-fuels. Lundholm et al. mixed the bio-fuels with peat, which greatly enhanced the initial agglomeration temperature for bio-fuels, and the results shown in Fig. 6. The results from varying the amount of peat fuel showed that adding as low as 5% of the Rojnoret Peat to bark from spruce prevented the bed from agglomeration up to above 1020 °C. Therefore, biomass co-combustion is a good method for preventing the agglomeration problem.

4.2. Bed agglomeration and deposit formation mechanisms

Ohman et al. presented that for major biofuels there is no major difference in layer formation processes or bed agglomeration mechanism between the two different operational modes (combustion and gasification) [71]. So the degree of deposits is mostly affected by the biofuels composition. Brus et al. [69] and Visser et al. [70] provided two different routes for agglomeration mechanisms: (i) "melt-induced" agglomeration, for bed materials directly glued together by a separate ashderived melt phase; (ii) "coating-induced" agglomeration, for the sequential process of coating formation on the bed particles, followed by adhesion and agglomeration. Coating-induced agglomeration has been sug-

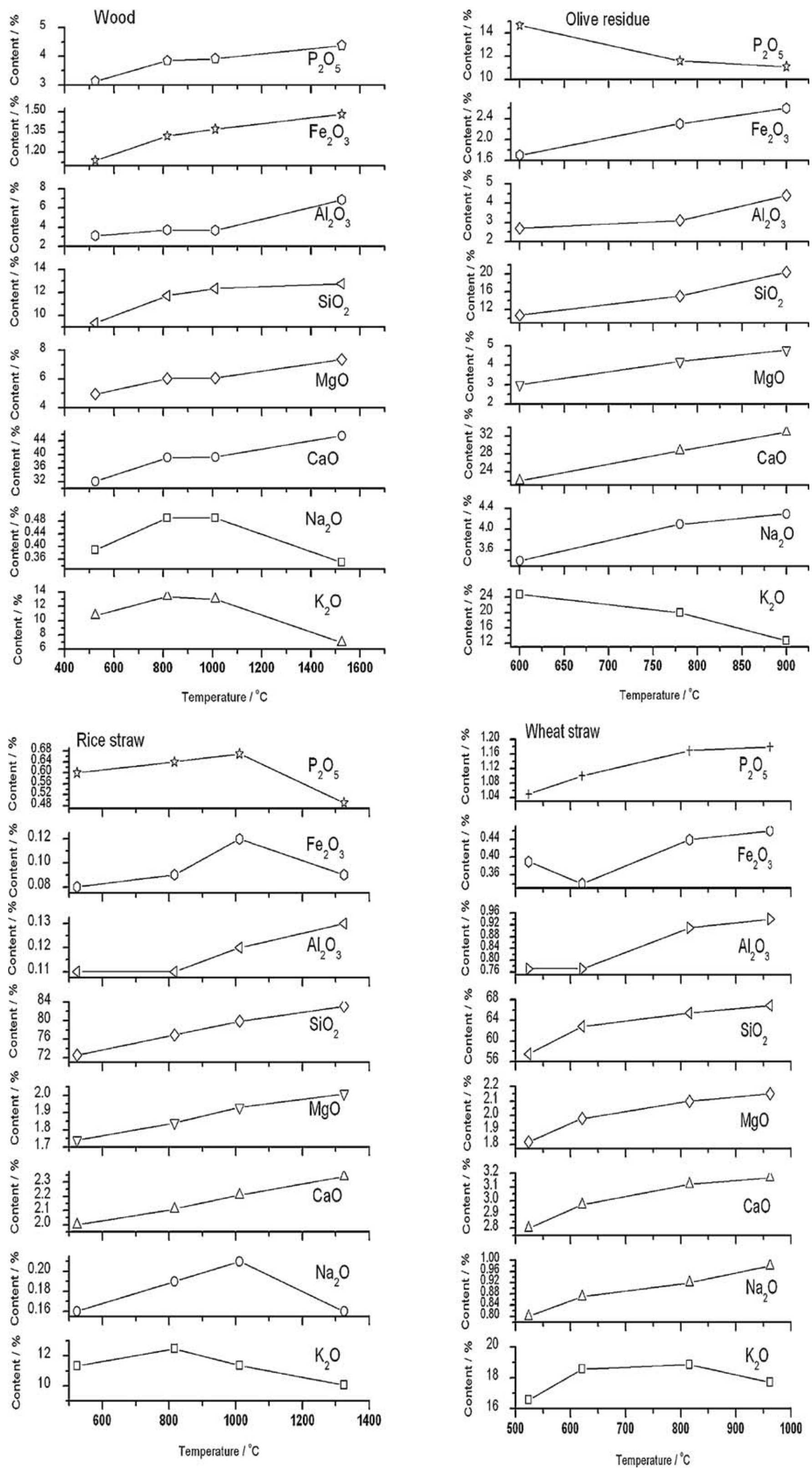


Fig. 3. High temperature elemental changes in common biomass ashes.

gested to be the main route for agglomeration during fluidized bed combustion of biomass fuel because the coatings may consist of compounds with low melting temperatures which can result in agglomeration of the bed material. Fig. 7 shows the process of biomass fuel coating-induced agglomeration.

Maria et al. [67] offered the bio-fuel element reaction mechanisms for agglomeration, which included two aspects: (1) Silicon reacts with potassium forming potassium silicates with a first melting point as low as some 750 °C. This may be the first layer formed on bed particles, which catches other small particles released

Table 5
Comparison ash composition after leaching pre-treatment.

Sample	K_2O	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	P2O5	SO_3	CL
Olive residue [47]	21.67	3.23	12.8	5.71	31.41	3.94	2.6	No	3.1	1.38
	8.44	0.05	17.95	6.8	39.6	0.62	3.21	No	1.51	0.05
Danish wheat straw [47]	23.99	5.22	2.7	1.73	27.96	3.43	0.59	No	3.83	12.77
	16.7	3.65	7.8	3.18	37.9	2.71	3.01	No	3.2	5.7
Olive kernel [53]	12.7	4.3	32.9	4.8	20.4	4.4	2.6	11.1	4.8	No
	2.7	0.6	33.0	3.7	21.4	4.4	7.9	2.3	4.4	No
Olive tree wood [53]	7.2	2.6	44.2	3.5	10	1.2	1.0	17.0	6.8	No
	1.5	0.1	52.3	2.7	2.7	1.4	2.1	1.5	2.6	No

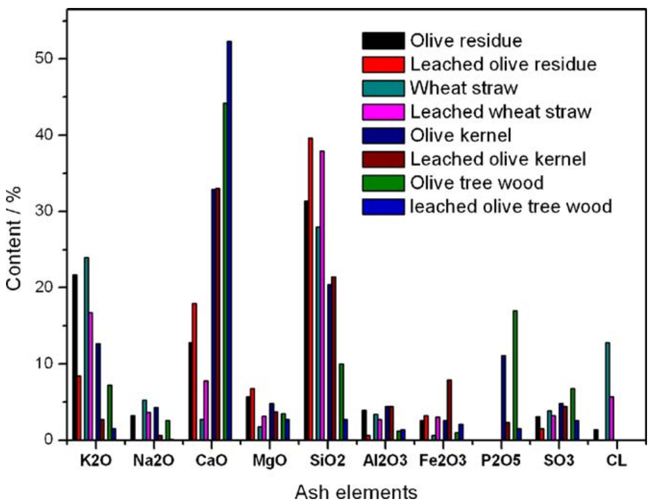


Fig. 4. Influence of leaching pre-treatment on bio-fuel ash composition.

from the fuel, such as calcium phosphates, sulfates, and oxides. After this first capture all components present can interact forming a sticky layer with a melting point below 800 °C. (2) Silicon reacts with calcium forming calcium silicates with a first melting point above 1000 °C. This second route is considered unlikely to cause agglomeration, due to the high first melting point, making capture of potassium components by gluing less probable at the low temperatures as in FBC. But for some especial bio-fuels, the agglomeration mechanism maybe is different. Bostrom et al. [63] think that there is a clear difference in the bed agglomeration mechanisms between phosphorus-rich fuels and phosphorus-poor

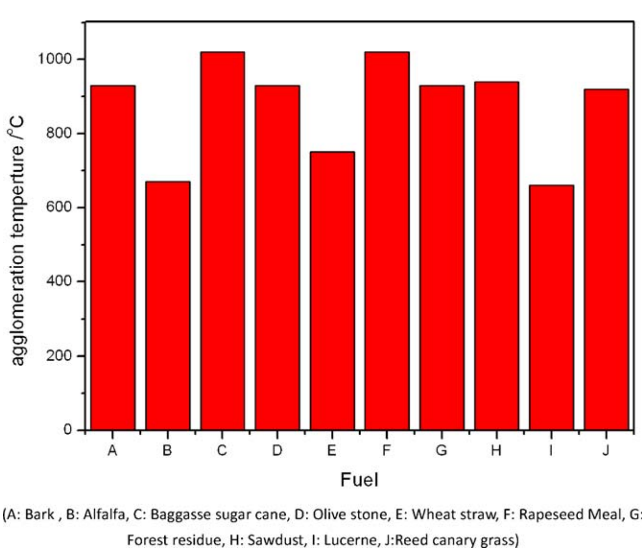


Fig. 5. Agglomeration temperature for different fuels.

Table 6
Initial agglomeration temperatures for the different fuels.

Bio-fuels	Agglomeration temperatures/°C
Bark (Scandinavian soft wood) [67]	930
Alfalfa [60]	670
Baggasse sugar cane [71]	1020
Olive stone [60]	930
Wheat straw (Danish) [61]	750
Rapeseed meal [59]	1020
Forest residue (soft wood) [67]	930
Sawdust [67]	940
Lucerne [71]	660
Reed canary grass [71]	920

biomass fuels. The ubiquitous continuous layers of bed grains in FBC combustion of woody biomass fuels was not seen in the phosphorus-rich fuels. Instead, very thin and discontinuous layers were observed together with isolated partly melted bed ash particles. The bed agglomeration mechanism is involved more of adhesion by partly melted ash-derived potassium–calcium phosphate droplets than direct attack of gaseous alkali on the quartz bed grains forming potassium–calcium silicate-rich bed grain layers.

4.3. Influence of additives on biomass ash deposits

Significant differences in agglomeration characteristics were found for the different minerals when bio-fuels were combusted. Some minerals can prevent the slagging trends in a certain extent. Geyter et al. discovered that potassium-feldspar was shown to

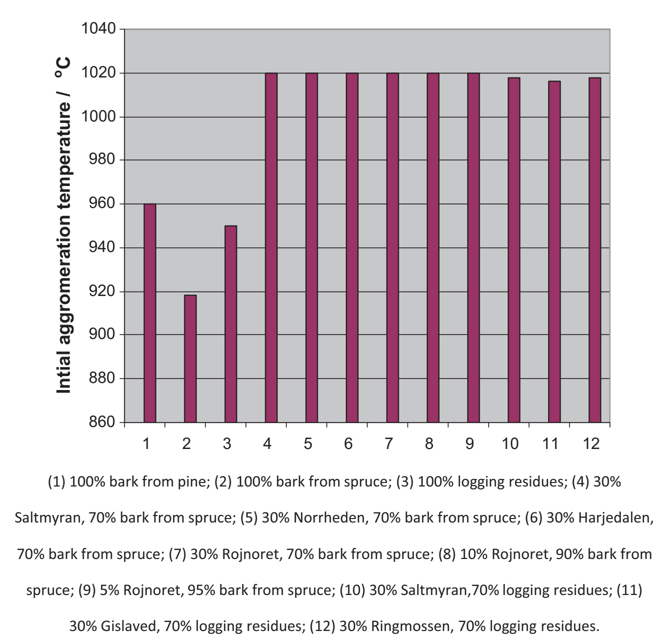


Fig. 6. Initial agglomeration temperatures for the different fuel mixtures, according to Lundholm et al. [68].

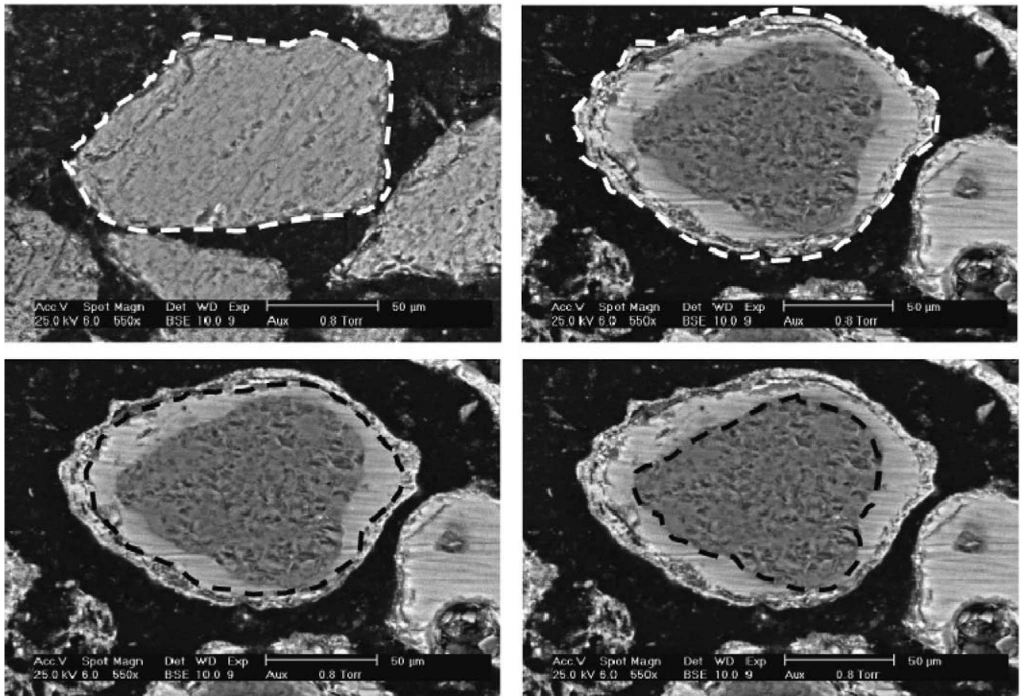


Fig. 7. Areas of unreacted bed particles (top left) were measured and compared to the areas of bed particles after 40 h combustion of olive residue (full size (top right), inner layer + quartz (bottom left), and quartz (bottom right)), according to Brus et al. [72].

lower the initial de-fluidization temperature for combustion of bark and olive residues. Plagioclase and olivine on the other hand were found to increase the initial de-fluidization temperature as compared to quartz for the combustion of olive residue, but for bark combustion, they did not differ significantly from quartz [66]. Bostrom et al. [64] thought that the effect of the kaolin additive on the formation of fine flue gas particles was an increased share of condensed K-phosphates at the expense of K-sulfate and KCl which can increase the initial agglomeration temperature. But the latter phase was almost completely absent in the particulate matter. Consequently, the levels of HCl and SO_2 in the flue gases increased somewhat. The following reactions were anticipated in producing as follows:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O$$

$$Al_2O_3{\cdot}2SiO_2 + 2KCl + H_2O \rightarrow 2KAlSiO_4 + 2HCl$$

$$Al_2O_3{\cdot}2SiO_2 + 2SiO_2 + 2KCl + H_2O \rightarrow 2KAlSi_2O_6 + 2HCl$$

Lindstrom et al. [58] also found that the addition of lime could reduce the formation of slag for barley and totally eliminated it for rye and wheat during the biomass combustion. This occurs because lime contributes to the formation of high-temperature melting calcium potassium phosphates. Pommer et al. reported that the effects of adding peat into forest residue combustion was an increased bed agglomeration temperature, a reduced amount of fine particles, and an increased amount of coarse particles [65]. Therefore, so to speak, in the bio-fuel combustion by adding some kind of additive is beneficial to prevent boiler slagging problems.

5. Biomass thermal conversion technology for phosphorus

Phosphorus is a limited non-renewable resource, which is indispensable as an essential nutrient for the growth of organisms in most ecosystems, and cannot be replaced by other elements. Apatite minerals are the main raw materials used in the manufacturing of phosphorus fertilizers. However, the resources of apatite are estimated to last only for about 200 years [72]. So the methods of recovery phosphorus used in the world are needed. One way of recovery phosphorus is from biomass ash because some biomass such as olive, sludge, meat and bone meal (MBM), and poultry litter, etc., contains considerable amounts of phosphorus. Biomass thermo-chemical processing is a major method for phosphorus recovery, which mainly includes three kinds of means. The first way is the biomass combustion for P rich in the ash as direct resource. The second way is a two-step thermal treatment including biomass combustion, and then the dry process ash for P recovery. The third way is also a two-step means including biomass combustion, and then the wet process (leaching) ash for P recovery.

5.1. *Phosphorus enriched in the ash by the biomass thermal conversion technology*

A strong enrichment of calcium, potassium, magnesium and phosphorus was observed for all the biomass samples [77]. The composition of sewage sludge ash is typical for municipal sludge ash. Silicon, iron, phosphorus, calcium and iron are the main components [75]. The results obtained in this work showed that the phosphorus is more concentrated in the fly ash than in the bed ash. Generally, 75–98% of the phosphorus leaving the CFB boiler is retained in the fly ash. Therefore, the development of a process for recovery of phosphorus should be focused on fly ash [73]. The fly ash was enriched in volatile sodium, phosphorus, and sulfur that had condensed on the surface of the fly ash particles [74]. Among the fly ash, seen from Fig. 8, if phosphorus recovery is the focus, the secondary fly ash should be studied in more detail with the bag-filter ash as a comparison [73]. Many elements were found in considerable concentrations in the fly ash, namely, aluminium, calcium, iron, potassium, magnesium, sodium, phosphorus and sulfur, although a range of trace elements were also identified [76]. A comparison of the molar ratios between Ca and P in the ashes shows that calcium is enriched relative to phosphorus during ash formation. However, the cyclone ash generally does not contain enough cal-

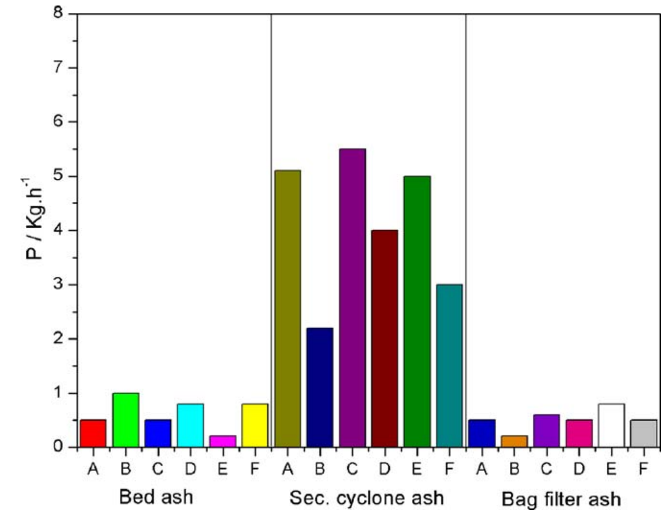


Fig. 8. Phosphorus flows in the different ashes as kg/h for the tests with 15% sludge as co-fuel [73] (A: Fe + no lime; B: Al + no lime; C: Fe + limestone; D: Al + limestone; E: Fe + hydr.lime; F: Al + hydr.lime).

cium to indicate that the phosphorus would be present in $Ca_3(PO_4)_2$ only [73]. The MBM ash contains large proportions of calcium and phosphorus in apatite forms with high melting points, as well as sodium, potassium and chlorine [78]. The presence of phosphorus in the MBM ash also contributes towards formation of low temperature eutectics with olive bagasse potassium, forming K_2PO_4 with melting point of approximately 800 °C [79].

5.2. Phosphorus distribution in the ash by the biomass thermal conversion technology

Fine particles are composed only of K, Cl, and S in the form of potassium sulfate and chloride except for the tests at 1450 °C, where phosphorus appeared also in significant amounts, although the species in which it was contained could not be determined exactly [86]. Phosphorus contents in the submicron particles were obtained in the experiments, confirming the key role of the bio-fuel in the production of the K, P, and Cl finally found in submicron particles [83]. The main components in the submicron ash are sulfur, silicon, sodium, and phosphorus, with sulfur being the most abundant element detected on the filters [89]. The value of [P]/[K] in the submicron particles presents its dependence on reactor temperature. It clearly shows that the relative importance of phosphorus within fine aerosols strongly increases with the combustion temperature, and [P]/[K] is zero at 1100 °C in fact [86]. The S and P concentrations increase with decreasing particle size [87]. In the case of sludge combustion, increasing oxygen content greatly enhanced the amount of P in the size range of 2.5–10 μm, suggesting the shedding of more of the inherent submicron particles from the char [90]. Becka et al. presented that the results of fuel and fly ash analysis showed an increased content of phosphorus during the co-combustion conditions. The analysis of the fine particulate matter showed a high phosphorus concentration on particles smaller than 0.9 μm. At the same time, a during coal combustion at plant, the largest share of particle bound phosphorus was also found at particle sizes below 0.9 μm [83]. On the other hand, SO_3 and P_2O_5 were prevalent in the small mode around 0.06 mm, which is formed by vaporization of these two elements. For other metals found in PM_{10}, the refractory metals were enriched in the large mode, with concentrations proportional to their content in the excluded minerals in the raw coal. Volatile metals were however enriched in the small mode since, they react with gaseous SO_2 and P_2O_5 to form sulfates and phosphates in the solid phase [88].

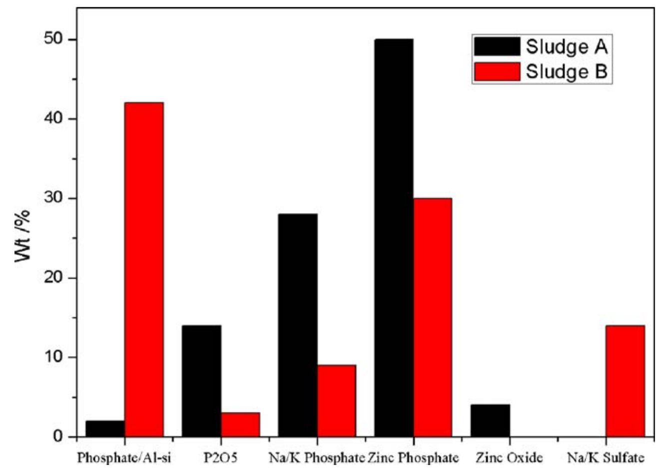


Fig. 9. Chemical forms of P in PM1 for the sludge combustion [102].

The chemical analysis of fly ash particle fractions with particle sizes below 0.05 mm showed high phosphorus concentrations which confirmed the presence of gaseous phosphorus in the flue gas [80,81], since these small particle fractions are primarily generated by nucleation of gaseous compounds [82]. A considerable phosphorus concentration on particle fractions smaller than 0.05 mm is a clear indication of the presence of gaseous phosphorus compounds [83]. The results show that the phosphorus concentration on the submicron particles is widely independent of the flue gas temperature. Derived reactions of flue gas particles with sub-micron calcium phosphates indicate a contribution to catalyst deactivation on usual operating temperatures [84]. Emission of airborne P-bearing particulates from combustion of both coal and sewage sludge samples has been studied in a lab-scale drop tube furnace. The results indicate that both the organically bound fraction of phosphorus and its inorganic species in a complex form containing Si, Al, Ca, Fe, P and O appear to vaporize readily. The phosphorus vapors undergo oxidation, chemical reactions with other metallic vapors including Na/K/Zn, nucleation, and homogeneous/heterogeneous coagulation to form a mixture of their oxides and phosphates with particle sizes smaller than 1.0 μm. On the other hand, phosphorus in the larger fractions, >1.0 μm, mainly consist of apatite and condensed melting phases, which may have been formed through the direct liberation of inherent apatite in raw fuels and the shedding of melting P-bearing particles from the char surface. The amounts of phosphorus in each fraction of PM_{10} vary considerably with fuel type and combustion conditions [85].

5.3. Phosphorus speciation in the ash by the biomass thermal conversion technology

Phosphorous, which is a significant component of the sludge, probably formed various phosphates with calcium, potassium and iron [91]. Stoichiometric considerations indicated that those particles were composed only by those two compounds and small amounts of phosphorus, probably present as potassium phosphate [98]. Especially in the sludge cases, phosphorous appears in the form of $Ca_3(PO_4)_2$ [92]. All phosphorus was assumed to be associated with the calcium, giving the 'inert' $Ca_3(PO_4)_2$ [93]. Phosphorus is also present dominantly as oxides (P_4O_{10} (g), P_2O_5 (g), PO (g) and PO_2 (g)), while H_3PO_4 is dominant at low temperature whatever the combustion conditions [94]. When phosphorus occurred, it occurred together with Fe, K and Ca which could be expected since these cations, especially Ca, have a strong tendency to form phosphates together with potassium [100]. In addition, Fe_2O_3, $Ca_9Fe(PO_4)_7$, $Fe_7(PO_4)_6$ were identified in the secondary cyclone

ash and Fe_2O_3 in the filter ash which also confirmed [101]. Zhang et al. reported some main chemical forms of P in Fig. 9.

Ca in MBM must be essentially present in bone fragments containing apatite mineral compounds; hence it is probably associated to phosphorus [95]. In the case of bones dominates calcium and phosphorus groups bonded to carbon as intercalates. In the case of vegetable rests the conjugated carbon chains, rests of sugar-like structures (C–O–C), rest of magnesium from chlorophyll bonded [96]. This small signal could be attributed to HPO_4^{2-} ions, confirming the presence of calcium deficient apatite $[Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}]$ as observed in IR analysis in the MBM [97]. From the SEM analysis of bed material we noticed that phosphorus was detected bound together with calcium in the bone material as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is a stable compound and does not decompose [99].

5.4. Phosphorus bio-availability in the ash by the biomass thermal conversion technology

According to Möller et al., 80% of the phosphorus is being transformed into apatite, which is unavailable to plants [104]. This has been claimed as a drawback, but Linderholm stated that only 0.01% of the phosphorus in the ground is accessible to the plants, and it is of little importance in which chemical form the phosphorus is added to the depot [103]. More ash analysis is needed before it can be stated whether the quota between phosphorus and heavy metals is higher or lower than in the phosphorus products from the fertilizer industry. If the quota were found to be acceptable, the ash could be considered for agricultural land as well forests [105]. The ash contains substantial amounts of phosphorus, which ought to be recycled to farmland in many cases in order not to lower the depot of phosphorus in the ground. Fire temperatures insufficient to volatilize mineral nutrients can result in an immediate increase in nutrient availability. Raison et al. found ashing resulted in increased concentrations of K, P, Mg, and Ca in the residual material [106]. K, Mg, and Ca are not readily lost due to their high volatilization temperatures (774, 1107, and 1484 °C, respectively). And while elemental phosphorus volatilizes at 280 °C and the predominant form in biological material, phosphate, sublimates at 360 °C, this material is largely retained in the residual ash [107]. Of the macronutrients (nitrogen, phosphorus, potassium, calcium, magnesium and sulfur), fly ash can supply sulfur, especially if it comes from the combustion of wood chips [30]. The MSW derived leachates had significantly higher levels of parameters that reflect biological activity including turbidity, organic carbon, nitrogen, phosphorus, volatile acids, iron, and manganese [108]. Re-burning of ash samples at 550 °C for 2 h increases the concentrations of Ca and K from 12% to approximately 18% and from 6.5% to 8.9%, respectively. Additionally, the concentration of phosphorus increases from 0.60% to 0.95%. The concentration of C org in the re-burned fly ash is 5%, and the pH and EC values are decreased. Additionally, it is possible to increase the dose of ash used for spreading so that suitable nutrient concentrations are achieved. However, by increasing the ash dose (e.g. in order to achieve desired amount of phosphorus) the amount of environmentally harmful elements and compounds that are applied on forest soil also increases [109]. Adam et al. [110] discovered that the P in the sludge ash exhibits low bioavailability, a disadvantage in farming. Therefore, in a second thermo-chemical step (dry process ash), P is transferred into mineral phases available for plants, and heavy metals are removed as well. The P-bioavailability was significantly increased during thermo-chemical treatment resulting in P-solubility in citric acid of up to 100%. Fig. 10 P-solubility of SSA untreated (raw ash) and thermo-chemically treated at different process temperatures by Adam et al. [110]

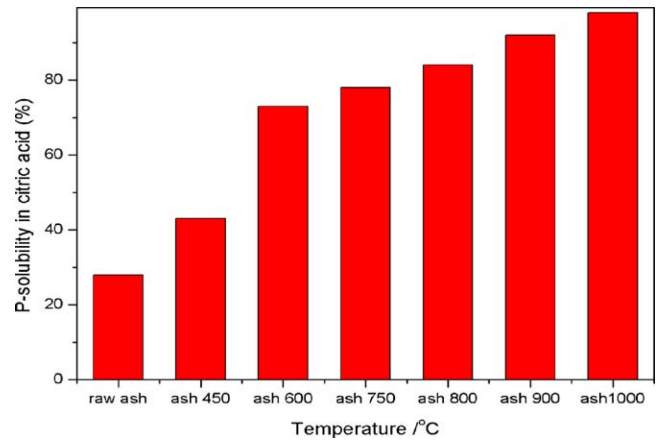


Fig. 10. P-solubility of SSA untreated (raw ash) and thermo-chemically treated at different process temperatures [110].

For the biomass such ash manure, it has been shown that the phosphorus in the ash after combustion exists in chemical structures less accessible to plants than in the manure, this is an especial condition [105].

6. Phosphorus recovery from ash by the different leaching technology

6.1. Phosphorus recovery by the bioleaching process

Loss of nitrogen and phosphorus has been reported while carrying out bioleaching of heavy metals from sewage sludge and soil–sludge mixtures [113,114]. Shanableh et al. reported the loss of 76% phosphorus and 38% nitrogen during sludge bioleaching [115]. With increase in solid content the sludge bioleaching was enhanced, which was represented by the acceleration of sludge acidification, oxidizing environment formation, and substrate (sulfur) utilization. Higher solid content was more efficient to solubilize the heavy metals and total phosphorus (TP) than lower solid content, while total nitrogen (TN) release was not influenced by solid content [111]. Solubilization efficiency of chromium, cadmium, copper and zinc from soil was 88, 93, 92 and 97%, respectively. However, loss of nitrogen, phosphorus and potassium from the soil was 30, 70 and 68%, respectively. Phosphorus solubilization is closely related to the sludge pH, especially, phosphorus is solubilized more rapid when pH decreases to 2.0 and below [112]. Wong et al. reported that at lower initial pH of the sludge, around 39% nitrogen and 45% phosphorus were lost, whereas the loss of nitrogen and phosphorus was found to be negligible at higher initial pH = 6 of the sludge [120]. Phosphorus leached out from soil was 1961 mg/kg during the first 2 weeks, accounting for a loss of nearly 40%. During subsequent weeks, soil was leached of 3527 mg phosphorus/kg, resulting in 70% loss. Phosphorus solubilization was found to be more rapid as pH decreased to 2.0 and below [112]. Highly comparable 76% phosphorus leaching from biosolids during bioleaching of heavy metals using sulfur oxidizing bacteria has been reported by Shanableh and Ginige [115]. Less than 15% of nitrogen and 6% of phosphorous were lost after 16 days of bioleaching when using FeS_2 as the energy source. Comparing to 39% and 45% loss respectively for these two nutrients when using $FeSO_4{\cdot}7H_2O$ as the energy source, FeS_2 appears to be a more suitable energy source for preserving nutrients in sludge while removing heavy metals from sludge [116]. In the present study, after bioleaching 32% nitrogen and 24% phosphorus were leached from the sludge using ferrous sulfate as a substrate, whereas only 22% nitrogen and 17% phosphorus were lost using ammonium ferrous sulfate [117]. Pyrites

can be oxidized by the bacterium acidithiobacillus ferrooxidans (At. f.), producing H_2SO_4 and $FeSO_4$. Rock phosphate is dissolved by H_2SO_4, forming soluble phosphorus. Fe^{2+} in $FeSO_4$ is oxidized to Fe^{3+}, producing energy to sustain the growth of At. f. The effects of four factors (rock phosphate dosage, pyrite dosage, culture temperature and time) on the fraction of phosphorous leached were investigated. It is suggested that the optimal conditions are as follows: rock phosphate dosage 1 g/L, pyrite dosage 30 g/L, and culture temperature 30 °C, culture time 84 h. The fraction of phosphorous leached is up to 11.8% [119]. Wong et al. further showed that around 15% of nitrogen and 6% of the phosphorus were lost from the sludge using FeS_2 and acidithiobacillus ferrooxidans [121]. However, such losses can be reduced by maintaining pH >2 or preferably 2–3 and the nutrient value of the sludge can be conserved while obtaining sufficient metal removal. This was also demonstrated by Blais et al. who reported that the acidification of the sludge to pH 1.5 resulted in a loss of 44% of total phosphorus, whereas at pH 2.5, the loss of total phosphorus was only 6% with the same sludge [122]. In this way, the aims of this study were to isolate and characterize phosphate-solubilizing bacteria associated to a high phosphorous iron ore located in the Brazilian region of Minas Gerais and to determine the mechanisms by which they solubilize phosphorous moieties. Phosphorus content of the ore material is 0.18% and, therefore, it is considered as a high-phosphorus iron ore. Among the culturable bacteria associated to the iron ore, four morphologically distinct bacterial strains showed high phosphate-solubilizing activity. Phosphate-solubilizing bacteria can supply plants with phosphorus from sources that are otherwise poorly available. Therefore, solubilization of phosphatic minerals by microorganisms is a research topic of significant interest to the agriculture sector due to its applicability in bio-fertilization [118].

6.2. Phosphorus recovery by the supercritical extractions

Sweden with expected requirements of phosphorus recovery, is working with development of methods to recover products from the supercritical water oxidation (SCWO) process and incineration [149,150]. The ion exchange process has however been difficult to accomplish and recovery by precipitation as iron phosphate has been considered. The use of SCWO combined with phosphorus recovery is under development as the Aqua Reci process [151]. Phosphate release from ash, dried sludge at 300 °C and SCWO residue showed similar results at 1 M acid leaching. However, it seems to be easier to release phosphate from the SCWO residue than from the ash at low acid concentrations. SCWO residue showed higher release than the other ashes at 0.5 M HCl. It was found that the pre-treatment of the ash may be important for better release of phosphate [152]. Many of the pollutants contain heteroatoms, such as chlorine or other halogens, sulfur and phosphorus which form acids during the SCWO process. These acids together with oxygen dissolved in supercritical water represent a highly corrosive fluid medium [153]. First, heteroatoms such as sulfur, chlorine or phosphorus lead to the production of the corresponding acids, respectively, H_2SO_4, HCl and H_3PO_4. Those acids can induce a corrosion attack of material especially under sub-critical temperatures [154]. Organic nitrogen is converted to molecular nitrogen and small amounts of nitrous oxide (N_2O), while organics containing sulfur, phosphorus or halogens form mineral acids [155,156].

For assay of the phospholipids phosphorus, ammonium the molybdate/malachite green reagent described by chalvardjian and rudnicki was used. 100 mg of extracted lipids in chloroform were evaporated. 50 mL of perchloric acid (70%) was added and tubes heated to 100 °C for 30 min to digest and liberate the organic phosphorus [143]. Phospholipids (PL) were successfully extracted from dried egg yolk by using neat supercritical carbon dioxide (SC-CO_2) on a micro-scale. The spray-dried egg yolk powder was extracted with SC-CO_2 at a density of 1.06 g/mL (517 bar, 40 °C), which was the maximum of density achievable with the apparatus. The extraction yield obtained by SC-CO_2 (67 g of extract per 100 g of sample) can be compared with the conventional bligh and dyer extraction method (63 g of extract per 100 g of sample), which involves a chloroform, methanol, water mixture as an extraction solvent. The solvent extract contained 29% of PL, while the neat SC-CO_2 extract consisted of 26% PL [144]. Chlorine and organophosphorus pesticides could obtained from spiked sand, the recoveries were poor (down to 27%) from standard reference materials (SRMs) [145]. The results were improved in later work when an average of 93% was recovered from spiked soils using a 3% methanol–carbon dioxide mixture. The addition of traces of water (either in the carbon dioxide or in the soil sample) showed an improvement, indicating that consistent sample preparation was very important [146]. Lecithin is not soluble in SC-CO_2, therefore, the oil extracted with CO_2 contains ten times less phosphorus than that present in crude oils [147]. The amount of phosphorus in the oil extracted from oats was considerably increased when oats were saturated with ethanol before SC-CO_2 extraction [148].

6.3. Phosphorus recovery by the chemical extraction

The phosphorus recovery technique with low consumption of chemicals allows utilization of the phosphorus in the ashes. Chemical extraction is a promising method for separating elements from sewage sludge ash by using chemicals to reduce the amount of elements present in the ash [164]. Hong et al. studied phosphorus recovery from waste-activated sludge incinerator ash and found that 2 mol/L HCl could leach phosphorus out of the ash but it could extract no more than 69% of the major metals content (Ca, Al and Fe). However, for phosphorus recovery, they recommended solvent extraction using organic solvents, which was thought to incur extra cost for the successful application of this system. Adsorption is one of the processes that can uptake phosphorus from dilute solutions and thus can be considered to be suitable for the recovery of dilute concentration of phosphorus [162]. Ash from thermally gasified piggery waste (GA) was treated with sulfuric acid (H_2SO_4) using two extraction methods. First different loads (0.39–0.98 kg H_2SO_4/kg ash) and concentrations (0.2–2 M) were used in 3 h extraction. Second, titration of 1:25 (w/w) ash: water suspension was conducted with 4 M H_2SO_4 to determine ash buffer capacity at nine pH steps from 12 to 0.1. Total P and zinc (Zn) dissolution was monitored. Optimal acid load and concentration to dissolve 94% P and 55% Zn from GA was 0.98 kg H_2SO_4/kg ash and 0.6 M, respectively, which corresponds to acid demand of 19.2 kg H_2SO_4/kg P recovered. Acid load had stronger effect on dissolution than concentration in the first method. However in the second, both factors had comparable effect [166]. The phosphorus leaching increased with the increase in acid concentration and temperature. Kinetic studies showed that the complete leaching of phosphorus took place in less than 4 h. Selective adsorption of phosphorus by using orange waste gel provided a hint for recovery of this natural resource, which eventually could meet the ever-increasing requirement for phosphorus. The overall results indicated that the incinerated sewage sludge ash can be treated with acid to efficiently recover phosphorus and thus can be considered a potentially renewable source of phosphorus [163]. When the ashes were leached at pH 2.5, only 22–30% of the phosphorus in the secondary cyclone ashes and 35–60% of that in the bag-filter ashes was dissolved. By decreasing the pH to 1, the phosphorus yield in the leachate of the secondary cyclone ash from sludge precipitated with aluminium sulfate increased to 74–95%, whereas 49–65% of the phosphorus in ashes from iron-based sludge could be extracted. Generally, at the pH 1, the phosphorus was easier extracted from the Al-rich ashes than from the Fe-rich ashes.

Table 7
Main phosphorus compounds in ashes and post-leaching residues [165].

Crystal phases	Ash calcined at temperature/°C							Post-leaching residue from ash calcined at temperature/°C						
	630	850	900	930	950	980	1000	630	850	900	930	950	980	1000
Calcite	+													
Anhydrite	+	+	+	+	+	+		+	+	+	+	+		+
Quartz	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Silica														+
$FePO_4$	+													
$Ca_9FeH(PO_4)_7$	+	+	+	+	+	+	+							
Meghemite							+							+
Hematite	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bessanite								+	+			+		
Albite											+		+	

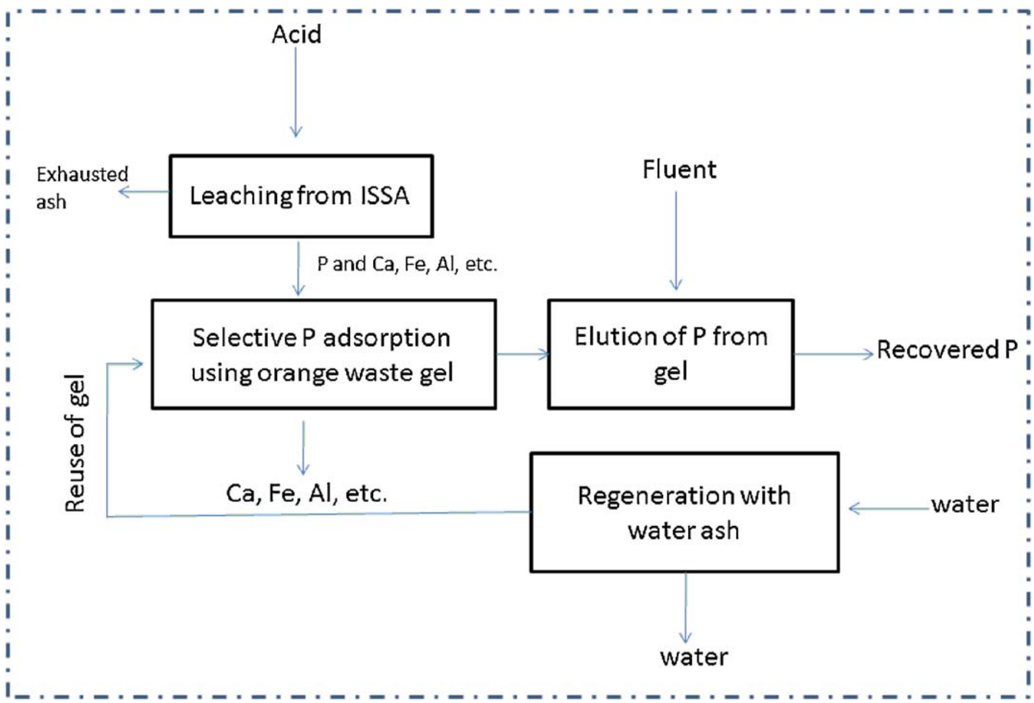


Fig. 11. The phosphorus recovery scheme from the sludge ash [163].

The results showed that it is possible to find a pH range (0.5–1) in which one can extract a significant fraction of the phosphorus from these ashes without precipitation of secondary phosphates [128].

The overall findings of this laboratory investigation confirmed a strong case for ISSA to be beneficially leached to recover phosphorus. This study indicated that phosphorus as well as other metal ions could be recovered from incinerated sewage sludge ash by using sulfuric acid or hydrochloric acid as the leach liquor. Quantitative leaching of phosphorus was achieved with an optimum condition as follows: 0.05 mol/L H_2SO_4 or 0.1 mol/L HCl at L/S ratio of 150 mL/g at 30 °C for 4 h of shaking. Since the application of sewage sludge in agriculture is going to decline, phosphorus recycling from the sludge ash becomes more and more pertinent [163]. That is, concentration of phosphorus in leachate increased with the leaching time in the first week, and then decreased with leaching time. After three-weeks of continuous leaching, concentration of phosphorus in leachate decreased to 0.01 mg/1, which is near the detection limit of the analytical method, and then remains nearly unchanged [161]. Temperature 950 °C of thermal processing of ash was found to be mostly advantageous for selective extraction of phosphorus compounds from the ashes with nitric acid, and Table 7 is the main phosphorus compounds in ashes and post-leaching residues [165].

Recovery of phosphorus from sewage sludge can also be carried out through an extraction procedure. In the KREPRO process, sludge is hydrolysed at 1401 °C and 3.5 bars, phosphorus compounds are dissolved along with other components of the sludge. In the BioCon process, the sludge is dried and incinerated with utilization of the heat from the combustion in the drying step. The ash is ground and extracted with sulfuric acid. The recovery of phosphorus from the liquid phase is carried out using ion exchange techniques. The KREPRO process and the BioCon process both have the disadvantage that the volumes of chemicals used are rather large and none of them has been implemented in a commercial facility [157,158]. Recently, a new process has been suggested: the SEPHOS process. In this process, sludge ash is treated with sulfuric acid at pH = 1.5. The solids are separated and the pH in the remaining filtrate is stepwise increased to pH 3.5 by addition of caustic soda to separate phosphorus and heavy metals. By the increased pH, the phosphorus is re-precipitated as aluminium phosphate [159,160]. In Fig. 11, it shows that the phosphorus recovery process from the sludge ash by the leaching technology.

7. Summary

To meet the growing energy demand and reduce the CO_2 emissions, the dependency in biomass for power generation and disposal of biomass ash will continue to increase. So how to utilize the biomass ash as a resource is more and more important. In view of the above discussion about phosphorus from biomass ash, the salient points from this extensive review could be summarized in the following sections:

(1) Biomass ash composition characteristics
  (i) Biomass ash mainly includes K, Na, Ca, Mg, Si, P, Al, Fe, S and so on elements, especially for alkali metal and alkali earth metal content prominent.
  (ii) The P content is very high in some biomass ash such as peach stone ash, sludge ash, MBM ash, etc.
(2) Biomass ash deposit properties
  (i) The initial agglomeration temperatures for most of bio-fuels were from 900 °C to 1000 °C.
  (ii) The coating-induced agglomeration has been suggested to be the main route for agglomeration during fluidized bed combustion of biomass fuel because the coatings may consist of compounds with low melting temperatures which can result in agglomeration of the bed material.
  (iii) It is beneficial to prevent boiler slagging problems in the bio-fuel combustion process by adding some kind of additive such as peat, etc.
(3) Biomass thermal conversion technology for phosphorus from the biomass
  (i) Phosphorus is mainly enriched in the ash by the biomass thermal conversion technology.
  (ii) Phosphorus is mainly distributed in the ash submicron particles.
  (iii) The ash P-bioavailability is significantly increased during thermo-chemical treatment.
(4) Phosphorus recovery from ash by the different leaching technology
  (i) The solubilization of phosphatic minerals by bio-leaching technology is important way to bio-fertilization.
  (ii) The supercritical extraction technology was found to be a good pre-treatment method for better release of phosphate in the biomass ash, but the expense is more high compare other technology.
  (iii) Chemical extraction is a promising method for separating elements from biomass ash.

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